REMOVAL OF ACRYLIC ACID FROM PROCESS WATER BY USING ACTIVATED CARBON BASED COCONUT SHELL

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ABSTRACT

The presence of Acrylic Acid (AA) in process water is the major problem in many industries which are using AA. There are no proper methods available to remove AA from process water and hence the industries incinerating the process water containing AA to remove it. This method consumes large amount of natural gas and in turn leads to high energy consumption. This research attempt to remove AA via batch adsorption process by using activated carbon based coconut shell. The process water that taken from BASF Petronas Chemicals Sdn Bhd containing 4 wt % of AA is used as sample water in this study. The adsorption capacity was tested by varying different size of activated carbon (granular and powder), amount of activated carbon and contact time. The initial and final concentration of AA was tested by using High performance liquid chromatography (HPLC). The performance of adsorption process is modeled using three types of adsorption isotherms namely, Langmuir isotherms, Freundlich isotherm and Redlich-peterson isotherm. From the experimental results it was found that the activated carbon based coconut shell was good in removing AA from process water and Langmuir isotherm describe the process well compared to other two isotherms with value R^2 = 0.94278 %. The maximum capacity of adsorption by using activated carbon based coconut shell was found, q_m = 94.3396 mg/g with the dosage used of 400 g/L. In addition to that, the adsorption of acrylic acid onto powder activated carbon represents the favorable process.

ABSTRAK

Kewujudan asid akrilik di dalam air proses menjadi masalah besar kepada industri yang menggunakan asid akrilik. Tiada method yang tepat dan betol untuk memisahkan atau mengeluarkan asid daripada ai proses. Sehubungan dengan itu, industri telah membakar air proses yang mengandungi asid akrilik dengan bertujuan untuk mengeluarkan asid akrilik tersebut. Kaedah pembakaran ini menggunakan gas asli dengan jumlah yang banyak dan seterusnya menyebabkan penggunaan tenga yang tinggi. Oleh itu, kajian ini bertujuan untuk memgeluarkan asid akrilik ini dibuang melalui proses penjerapan secara berkumpulan dengan menggunakan serbuk karbon diaktifkan berdasarkan tempurung kelapa. Asid akrilik yang digunakan dalam kajian ini adalah dari air proses yang diperoleh daripada BASF Petronas Chemicals Sdn Bhd mengandungi asid a sebanyak 4 peratusan berat. Kepekatan awal dan juga kepekatan akhir asid akrilik telah dikaji dengan menggunakan kromatografi cecair prestasi tinggi. Keberkesanan proses penjerapan ini dimodelkan dengan menggukan tiga jenis penjerapan sesuhu model iaitu Langmuir, Freundlich dan juga Redlich-Peterson (R-P). Daripada kajian ini,keputusan menunjukkan bahawa serbuk karbon diaktifkan berdasarkan tempurung kelapa adalah bagus dalam mengeluarkan asid akrilik daripada air proses dan Langmuir sesuhu adalah model yang palig sesuai berbanding dengan sesuhu model yang lain dengan nilai sebanyak R^2 = 0.94278 %. Maksimum kapasiti penjerapan dengan penggunakan serbuk karbon diaktifkan telah dijumpai iaitu sebanyak 94.3396 mg/g dengan jumlah carbon teraktif yang digunakan sebanyak 400g/L. Tambahan itu lagi, keputusan menunjukkan bahawa penjerapan process asid akrilik terhadap serbuk karbon diaktifkan adalah menggalakkan.

TABLE OF CONTENTS

CHAPTER 4 RESULT AND DISCUSSION

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

^{o}C	degree Celcius
%	Percentage
C_0	Initial concentration
C_e	Equilibrium concentration
g	gram
g/L	gram per liter
mg	Miligram
mL	mililiter
q_m	Maximum capacity of adsorption
R^2	Correlation Coefficient

LIST OF ABBREVIATIONS

AA	Acrylic acid
AC	Activated carbon
ACGIH	American Conference of Governmental Industrial Hygienists
C	Carbon
GAC	Granular activated carbon
H	Hydrogen
HPLC	High performance liquid chromatography
IUPAC	International Union of Pure and Applied Chemistry
N	Nitrogen
O	Oxygen
PAC	Powder activated carbon
ppm	Part per million
rpm	revolution per minute
S	Sulfur
TFA	Trifluoroacetic acid
Wt %	Weight percentage

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

In conjunction with rapidly changing technologies in Malaysia, there are increasing in amount of industrial company that directly will increase the amount of industrial products and as well wastes generated. In the industrial, the water is widely used especially in the process site that known as process water. Besides can be recycled in the process, process water also may discharge from the factory. When the process water is discharged, these not only could threaten the animals but also society's health as well environment. In addition to that, sometimes, the process chemicals mixed with process water and thus it is necessary for the industries to remove these chemicals before this process water is recycled or discharged as waste water.

The process water taken from BASF Petronas Chemical Sdn. Bhd., Gebeng, contains a lot of chemical components with different amount of weight percentages. In this process water, acrylic acid (AA) contains with high weight percentage compared to the other components. Acrylic acid with IUPAC name of prop-2-enoic acid is the simplest unsaturated hydrocarbon compound. It is a valuable industrial product that used for various important purposes in chemical factories. AA is widely used in many industrial processes and also consumer product. It is include detergent, paints, coating, synthetic fibers, adhesive and others (Kumar *et al.*, 2010). Acrylic acid is completely soluble in water and soluble in certain organic compound such as hexane, benzene. Because of having solubility property, an acrylic acid will cause harm for the water. Besides that, the amount of production acrylic acid cannot achieve the target of production.

Therefore, in order to remove the acrylic acid in the process water, it needs to be treated first before it discharged which called as water treatment. Water treatment can be divided into three types which are physical treatment, chemical treatment also biological treatment. The physical treatment can divided into screening, sedimentation, flotation, granular medium filtration. While for chemical treatment it is divided into chemical precipitation, adsorption, disinfection, dechlorination, ion exchange and other chemical applications. The biological treatments are done by treating with activated sludge process, aerated lagoon, trickling filters and biological nutrient removal. Besides that, the other methods such as coagulation-flocculation, electrochemical oxidation and membrane filtration also can be used in order to treat the unwanted contaminants in water.

For the treatment purpose by using physical treatment such adsorption process which used the adsorbent to adsorb unwanted contaminants in water. There are several adsorbents can be used such clay (Blockhaus *et al.*, 1997 and Hameed, 2007), alumina (Mao and Fung, 1997; Malgat *et al.*, 2004 and Roostaei and Tezel, 2004), silica gel (Roostaei and Tezel, 2004), alginate bead (Kim *et al.*, 2008), as well as activated carbon (AC) (Kumar *et al.*, 2008; Kim *et al.*, 2008; Kumar *et al.*, 2010 and Rivera-Utrilla *et al.*, 2011). The activated carbon adsorbent has been proved as an effective adsorbent in order to remove variety of organic and inorganic pollutants that dissolved in aqueous solution or from gaseous environment (Roostaei and Tezel, 2004; Dias *et al.*, 2007; Hameed *et al.*, 2008; Yuen and Hameed, 2009; Rivera-Utrilla *et al.*, 2011; and Kushwaha *et al.*, 2011). This adsorbent is considered as an effective adsorbent because of the properties like micro-porous nature, large surface area and others.

In the adsorption process whether kinetic process or isotherms process there are several models has been used to prove whether the process is acceptable or vice versa. For instance, there are Langmuir isotherms, Freundlich isotherm as well as Redlich-Peterson (R-P) equilibrium isotherm models have been reported by previous study (Kumar *et al.*, 2008; Kim *et al.*, 2008; Kumar *et al.*, 2010; Hameed *et al.*, 2008 and Ignatowicz, 2011).

1.2 PROBLEM STATEMENT

Acrylic acid is a compound that soluble in water (Kumar *et al.*, 2010) and also in several organic compounds such as alcohol, benzene, chloroform, ether, and acetone. Besides that, the acrylic acid that released in water will undergo microbial degradation, chemical and also photochemical reactions. At higher concentrations, it can affect human, living things and also the environment. Because of the solubility characteristic, the production of acrylic monomer is lower than the actual target of production.

In this research, the process water from BASF Pertronas Chemical Sdn. Bhd. not only contains the acrylic acid, but contains also the other compounds. Based on the data given on the BASF Pertronas Chemical Sdn. Bhd. process water, besides contain acrylic acid, there are also 23 others components present in this water. In this process water, the composition of water is approximately 87 weight percentage (wt %) and AA has the highest amount which is 4 wt %, followed with the other compounds like acetic acid, formaldehyde, maleic acid anhydride and others.

Currently, BASF Petronas Chemical Sdn. Bhd. is incinerating the process water to remove the acrylic acid and also other compounds that present in the process water. This incineration process consumes large amount of natural gas. So that, the removal of acrylic acid from process water will reduce the natural gas consumption and in turn will increase the profit of the process.

Therefore, this research is aims to attempt the removal of acrylic acid by using adsorption technique. Adsorption process by using activated carbon as adsorbent provides low cost and more efficient in this treatment process (Dias *et al.*, 2007 and Acharya *et al.*, 2009). According to Acharya *et al.* (2009), commercial activated is usually used but because the price is expensive, there is a new alternative by producing activated carbon from the raw materials like agricultural waste. For instance, raw materials that has been used are palm kernel shell (Jumasiah *et al.*, 2005), bituminous coal (El Qada *et al.*, 2006), sawdust, baggasse (Ionnidou and Zabaniotou, 2006 and Gratuito *et al.*, 2008), nut shells and peat (Yang *et al.*, 2010) as well coconut shell (Sekar *et al.*, 2004; Amuda *et al.*, 2007 and Ignatowicz, 2011)

1.3 RESEARCH OBJECTIVES

The purposes of this research are:

i. To remove acrylic acid from process water by using activated carbon based coconut shell.
ii. To study the adsorption isotherms

1.4 SCOPES OF STUDY

In order to achieve the research objective, the scopes that considered are as below:

i. The effect of activated carbon dosage.
ii. The effect of contact time.
iii. The effect of particle types of activated carbon

1.5 SIGNIFICANCE OF STUDY

The presence of acrylic acid in high concentration and higher toxicity can cause harm for environment and also human. So, treatment by using activated carbon can reduce the pollutions as well negative effects to the human, living things, and also environment.

Besides that, the water can recycle again in the plant and provide low cost for treatment process. It is because, by using a suitable activated carbon, it will indirectly reduce the cost of removal process. In addition to that, the production of acrylic acid will approximately achieved the factory's target by using desorption method to get back an acrylic acid.

1.6 DEFINITION OF KEY TERMS

Table 1.1: Definition of key terms

Terms	Definition
Hydrocarbon	Any class of organic compound which contains only of carbon and hydrogen atoms.
Unsaturated hydrocarbon	An organic compound that contain either double or triple carbon-carbon bonds.
Adsorbent	A material that has a capacity or tendency to adsorb other substance.
Adsorbate	A substance that has been or is capable for being adsorbed.
Adsorption	A chemical process that take places when a liquid or gas (adsorbate) accumulates on the surface of a solid (adsorbent), forming a molecular or atomic film

CHAPTER 2

LITERATURE REVIEW

2.1 ADSORPTION PROCESS

Adsorption process is known as attachment process of a substance either in gas phase or liquid phase to a solid particle. This process is occur when the gas or liquid phase substance are accumulates on the surface of solid. The solid that used is named as adsorbent. Meanwhile, substance that attached to the solid is known as adsorbate. There are a lot of advantages by using adsorption process when compared to the other process which are this process does not cause any pollution or harm for the system, easily regenerative and low cost of process.

2.1.1 Mechanism of Adsorption Process

In the adsorption process, it can be divided into three steps. These steps are started with the diffusion of a molecule to the adsorbent surface or across the liquid film surrounding the adsorbate particles. For example, it is known as external diffusion or film diffusion. Then, it followed by the migration from the external surface into the pores of adsorbent. In the other term, the second step occurs by diffusion of in the liquid contained in the pores or along the pore walls. This migration called as internal diffusion or also known as intra-particle diffusion. Lastly, the process is proceeding with the adsorption or desorption process between adsorbate and active site. In addition to that, monolayer is buildup of the adsorbate. The monolayer occur when the adsorbent is saturated which can’t adsorb anymore of the molecule.

The figure 2.1 exhibits the mechanism of the adsorption process that occurs onto solid particles.

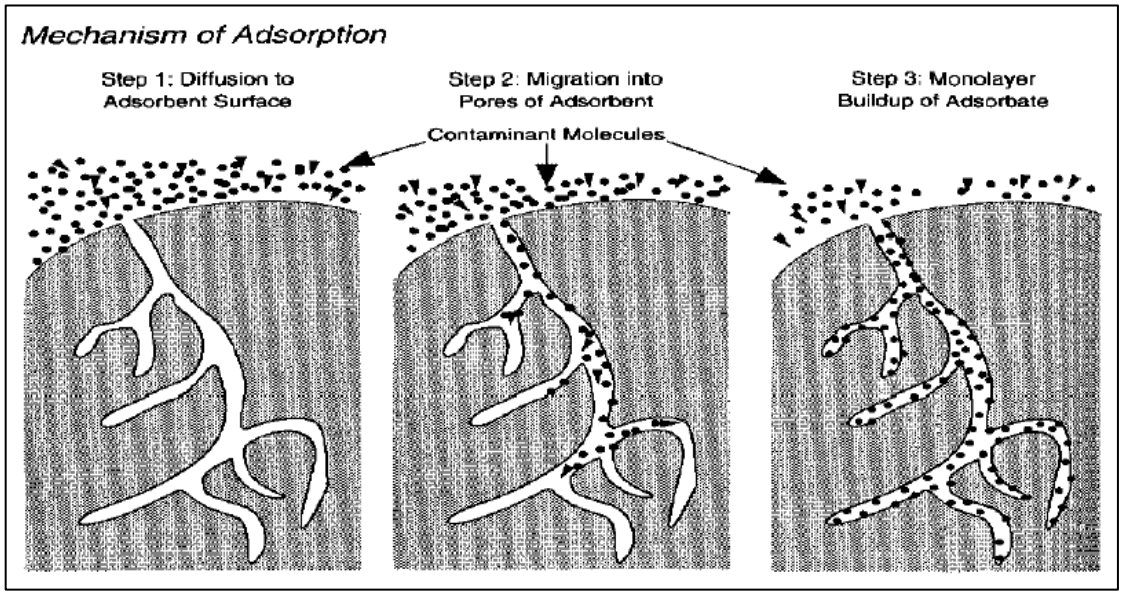

Figure 2.1: Mechanism of adsorption process

Source: Athappan (2008)

2.1.2 Types of Adsorption

Adsorption process can be divided into two types which are physical adsorption and chemical adsorption. The physical adsorption process will occur when the bonds exits between an adsorbate and adsorbent is weak which is the bonding occur from the van der Waals forces. For example of weak bonding is van der Waals, hydrogen bond as well dipole-dipole bond. For this type of bonding, this may cause the bond between adsorbate and adsorbent easily to broken if there is heating process of adsorbent or reducing the pressure are occurs.

Meanwhile, the chemical type of adsorption contains very strong bonding between the adsorbent and adsorbate. This strong interparticle bond occurs between adsorbate and adsorbent is due to an exchange of electron. For instance are ionic bond

and covalent bond. Therefore, with strong chemical bonding, the adsorbent used cannot be recovered again.

2.1.3 Factor Affecting Rate of Adsorption

In the adsorption process, the factors like particle sizes, surface area, temperature, and pH may affect the rate of process to occur.

2.1.3.1 Size of Particle or Molecular Size

Size of particle that may determine also as molecular weight of the particles is one of the factor and sources of energy for the movement purpose of particles. At a given temperature, the particle with smaller molecular weight or smaller molecules are able to move faster compared to the particle that has high molecular weight. Therefore, the rate of adsorption of smaller particles is faster compared to the largest one.

2.1.3.2 Surface area

Surface area of the adsorbent is also one of the important parameter that able to affect the adsorption rate. The surface area is directly proportional to the rate of adsorption. This means that, when the surface area in larger, the rate of adsorption is high. This is due to the large surface area contact occurring between adsorbate and adsorbent (Acharya *et al.,* 2009 and Kumar *et al.,* 2010).

2.1.3.3 Temperature

Adsorption process that taking placed usually in exothermic condition, which is releasing heat. The rate of adsorption process is indirectly proportional to the temperature supplied during the adsorption process. This mean, when the heat supplied is increase, the energy of the particles also increase as well this will increase the kinetic movement of the particles. Therefore, with the increasing of temperature, the rate of adsorption will decrease (Mao and Fung, 1997; Kumar *et al.,* 2008 and Kumar *et al.,* 2010).

2.1.3.4 pH

pH may determined as the degree of ionization process. This means that pH will determine either the solution is strong or weak of acid or base respectively. pH generally give inversely impact on the rate of adsorption which mean when pH value is lower, the rate of adsorption is increase (Hameed *et al.,* 2008 and Kim *et al.,* 2008).

2.2 ACTIVATED CARBON

2.2.1 History of Activated Carbon

Most of all materials able to contain high carbon content which has the potential to be activated. Activated carbon start used in a long time ago. It is started used in 1500 BC when Ancient Egyption followed by Hippocrates used it as an adsorbent for medicinal purpose, purifying agent and also to remove odor. According to Bansal and Goyal (2005), an Ancient Hindu used charcoal or namely activated carbon for water filtration.

During First World War, the application of activated carbon used as a gas masks as a protection from hazardous gases and vapors. According to David (2005) in Shaharuddin (2009), the application of activated carbon is used widely in a various industry.

2.2.2 Types of Activated Carbon Based

In order to use activated carbon as adsorbent, there are a lot of types of activated carbon that has been determined. Usually the commercial activated carbon is used in adsorption process such in adsorption of micro pollutants or heavy metals (Dias *et al.,* 2007), removal of acrylonitrile (Kumar *et al.*, 2008), treatment of synthetic dairy wastewater (Kushwaha *et al.*, 2011). But due to the high and expensive of production, there is the new alternative which is produce activated carbon from the wastes that will produce a lower price of production (Hameed *et al.*, 2008 and Kumar *et al.,* 2008).

The activated carbon can be produced from different raw material such as such sawdust, baggasse (Ionnidou and Zabaniotou, 2006 and Gratuito *et al.*, 2008), nut shells and peat (Yang *et al.*, 2010), bituminous coal (El Qada *et al.*, 2006), rice husk ash, bagasse fly ash, coal fly ash, straw dust (Kushwaha *et al.*, 2011), apricot stone (Kobya *et al*, 2005), palm kernel shell (Jumasiah *et al.*, 2005), Besides that, coconut shell also has been noticed as the raw materials in the production of activated carbon (Sekar *et al.*, 2004; Amuda *et al.*, 2007 and Ignatowicz, 2011)

Table 2.1 below indicates the differences between various types of activated carbon such coconut, coal, lignite as well as wood activated carbon and the comparison of these activated carbons in the characteristic of size either micropores and macropores, hardness, amount of ash, the solubility of activated carbon in water, dust, the reactivations level and lastly on the apparent density.

Table 2.1: Several types and properties of activated carbon

Properties	**Coconut AC**	**Coal AC**	**Lignite AC**	**Wood AC (Powder)**
Micropore	High	High	Medium	Low
Macropore	Low	Medium	High	high
Hardness	High	High	Low	n/a
Ash	5 %	10 %	20 %	5 %
Water soluble	Good	Low	High	medium
Dust	Low	Medium	High	n/a
Reactivation	Good	Good	Poor	None
Apparent density	0.48 g/cc	0.48 g/cc	0.4 g/cc	0.35 g/cc
Iodine Number	1100	1000	600	1000

n/a – not available

Source: Carbochem (2009)

Based on the table above, it generally shows that activated carbon based on coconut more effectives compared to the other types of activated carbon. This can be

seen according to the size of micropores of AC. Besides that, it also has good property soluble in water as well has high reactivation. According to Ignatowicz (2011) and Wei *et al.* (2006), activated carbon based coconut shell has properties of high surface area as well as larger adsorption capacity. It also contains the lowest percentage of ash where this contributes to the excellent property in adsorption process. This means, the amount of adsorption and the effectiveness of adsorption process by using coconut activated carbon is higher compared to other types of activated carbon.

In addition to that, when looking on the activated carbon based on coal and wood, the reactivation level of coal and it less soluble in water. Meanwhile, the reactivation of activated carbon based wood is too less or can be described as no reactivation. These two types of activated carbon have low surface areas as well as lower or poor properties in adsorption process. This has also has noted by Ignatowicz (2011) which state that the effectiveness by using activated carbon based on coal and wood is lower.

2.2.3 Properties of Activated Carbon

The adsorption capacity of activated carbon is related to its surface area, pore structure, and surface chemistry. (Ayranci *et al.*, 2005). All the activated carbon is divided into three types of pore sizes which are micropores, mesopores as well as macropores (Cameron Carbon, 2006). But, the size of micropores, mesopores and macropores of activated carbon is different between the others which are according on the types of raw material used in the production of activated carbon. This means that, different raw material used will produce different size of micropores, mesopores as well macropores of activated carbon.

The size for micropores is less than 40 Angstroms (Å), mesopores is in the range between 40 until 5000 Å and lastly is macropores is more than 5000 Å which is usually in the range of 5000 until 20000 Å (Cameron Carbon, 2006). Meanwhile, Wan Daud and Wan Ali (2004) have stated that the pore size for micropore is less than 2 nm or 20 Å, mesopores in between 2 until 50 nm and lastly macropore more than 50 nm. The

value of micropres, mesopores and macropores that stated by Wan Daud and Wan Ali (2004) is little difference and smaller when compared to the value stated by Cameron Carbon (2006). According to the sizes of pores having by activated carbon, the effectiveness of activated is higher when the amount of micropores size is large.

Therefore, in order to choose the suitable activated carbon used in the adsorption process, besides by choosing the lower cost of activated carbon, there are characteristics like iodine number, surface area, apparent density, types of particle size, and also ash contents needs to be considered (Carbochem, 2009).

The iodine number is the basic parameter that used to characterize the performance of activated carbon. Besides that, the iodine number is a parameter for the measurement of the activity level of activated carbon which is the level of activated carbon's activity is directly proportional to the iodine number having in the activated carbon.

Besides that, surface area of the particles also considered in the measurement for capacity of adsorption. The adsorption capacity of activated carbon is directly proportional to the surface area where when surface area is increase, the capacity of adsorption is increase. This is happen because, with the large surface area, there are more contact surface occurs between the adsorbent and adsorbate which this will make more adsorption occur.

In addition to that, the other parameter is apparent density. Density can be determined by mass of particle divided with volume or it also can be calculated by specific gravity of matter multiply with the volume of water which is 1000 kg/m^3. In choosing suitable activated carbon, the activated carbon with higher density will provide a greater volume of activity. Therefore, the quality of adsorption process also directly proportional to the density of that activated carbon.

Besides that, the type of particles which is the particle size of activated carbon whether granular, powder, pellet or else. According to Carbochem (2009) and Kumar *et al.,* (2008), matter with smaller particle size will provide high adsorption rate compared

to the particle having larger particle size. The adsorption rate occurs higher with smaller size of particle because of the reduction of the required contact time between the adsorbent with the adsorbate.

Last but not least is the content of ash containing in activated carbon. Ash content means the mass of incombustible material that remain after combustion or burning process for a coal samples as the percentage of the original mass of the coal. Higher ash content in the activated carbon has a tendency to reduce the overall activity and reduce efficiency of reactivation level of the activated carbon. This means that the adsorption rate of the activated carbon that contains higher ash content is lowest.

2.2.4 Classification of Activated Carbon

When jump into the classification of activated carbon, it can be classified into powdered activated carbon (PAC), granular activated carbon (GAC), extruded activated carbon (EAC), impregnated carbon, and others. Most previous researchers used powder type of activated carbon (Kumar *et al.*, 2008; Kim *et al.*, 2008 and Kumar *et al.*, 2010) and granular activated carbon (Kumar *et al.*, 2008) for the research purpose especially in the uptake of unwanted constituents in desired solutions.

The size for powder activated carbon is less than 1.0 mm with average diameter between 0.15 mm and 0.25 mm. Meanwhile, granular activated carbon, GAC has a larger particle size compared to the PAC. For the extruded activated carbon (EAC) consist a cylindrical shaped with diameters from 0.8 mm to 40 mm. This is has high mechanical strength and low dust content.

All the types of this activated carbon have different characteristics that will affect the adsorption rate in the adsorption process. Figures 2.2 indicate the illustration of the powder activated carbon.